Surface Oxide State on Metal Powder and its Changes during Additive Manufacturing: an Overview

E. Hryha, R. Shvab, H. Gruber, A. Leicht, L. Nyborg

Quality and usefulness of the powder for additive manufacturing (AM) are strongly determined by the surface composition of the powder. In addition, taking into account harsh conditions during AM process, significant changes in the powder surface chemical composition are taking place, limiting powder recyclability. Hence, knowledge concerning amount of oxides, their composition and spatial distribution on the powder surface determines further powder recycling. This communication summarizes possibilities of qualitative and quantitative analysis of powder surface chemistry by surface-sensitive chemical analyses using XPS and HR SEM coupled with EDX. The effect of alloy composition, AM process applied and powder handling on the surface composition of the powder are addressed. Results indicate significant enrichment in the thermodynamically stable surface oxides in case of high-alloyed powder for both, EBM and LS processes. A generic model for the oxide distribution, depending on the alloy composition and powder surface degradation during AM manufacturing, is proposed.

KEYWORDS: LEGHE ...

INTRODUCTION

The metal powder is the base material for powder bed or blown powder additive manufacturing technologies. At the same time, there is a lack of understanding of the effect of powder properties on the properties of the AM fabricated components, processability of the powder by specific AM process, AM process robustness, etc. Nowadays most powder for AM applications is produced by Electrode Induction melting Gas Atomization (EIGA) or Vacuum Induction Gas Atomization (VIGA), characterized by high-purity but at the same time high cost as productivity is low and manufacturing costs are high. In order to improve process efficiency and taking into account high cost of the powder, powder is typically recycled. At the same time, there is limited understanding of the powder degradation during AM process. Hence, typically applied industrial approach when it comes to the powder degradation are based on empirical approach developed by each user in-house based on the components manufactured, hardware utilized as well as alloys of interest.

Metal powder used for AM is characterised by a surface area that is about 10 000 times larger than the surface area of the bulk material of the same mass. This results in the significantly higher surface reactivity of the metal powder in comparison with the bulk metal. Reactivity is increasing with increasing surface area/decreasing particle size. At the same time it is important to emphasize that the pure metallic surface does not exist at ambient conditions – metallic surfaces are covered by surface oxide as well as absorbed species in order to minimize their surface energy. Hence, surface of the metal powder is typically covered by nanometre thick oxide layer that has a complex structure and composition [1-4]. Characteristics of the surface oxide formed are determined by the thermodynamic stability of the oxides formed by the metal/alloy as well as the history of the metal surface exposure to the surrounding conditions during powder manufacturing and handling [1-7]. Temperature and time of the exposure in combination with the oxidation potential of the surrounding atmosphere determines thickness, structure and composition of the oxide formed on the powder surface. Oxide stability itself has an important effect on the extent of the surface oxide formation during manufacturing and handling – better powder passivation in case of reactive powders as e.g. Al, Ti, etc. At the same time, stability of the surface oxide present determines behaviour of the powder during processing as well as type and risk of the defects formation. Therefore, knowledge concerning surface chemistry of the powder and its changes during AM processing is of vital importance in order to establish required powder manufacturing,

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handling and recycling routines for a specific alloy and AM technique.
The aim of this study is to demonstrate the application of the advanced microscopy and surface analysis methods for analysis of the metal powders for additive manufacturing. Focus is placed on powder bed methods – laser sintering (LS) and electron beam melting (EBM). Surface composition for different kinds of metallic powder with respect to material type and alloy composition are presented. Changes in surface oxide chemistry of the powder during AM processing as well as powder handling are discussed.

Experimental Procedure

Focus is placed on stainless steel 316L and nickel based superalloy powder Hastelloy X, produced by VIGA, and nickel based superalloy powder Alloy 718, produced by plasma atomization. Powder samples were prepared by lightly pressing the powder onto soft aluminum plates. Chemical analysis of the powder surface was performed by means of X-ray photoelectron spectroscopy (XPS), using PHI 5500 instrument. The analyzed area during XPS analysis was about 0.8 mm in diameter and thus a large number of particles (~100 particles) were analyzed at the same time, giving statistically reliable average result. Composition of the surface compounds was estimated by curve fitting of the characteristic peaks, and their intensities were corrected using standard relative sensitivity factors. Quantification of the results was performed by calibration measurements on pure elemental standards. Determination of the surface oxide layer thickness and compositional profiles was done by alternating ion etching and XPS analysis. Evaluation of the thickness of the surface oxide layer was performed using theoretical model involving the effect of the setup geometry (etching and measurement angles) with respect to the surface geometry (roughness) on the etching profiles and integrated in the software "Powder XPS calculator v.1.2.4", developed by authors for powder analysis [8]. The etching was performed in argon gas with an accelerating voltage of 4 kV giving an etching rate from 3 to 5 nm·min^{-1}. Surface oxide distribution and morphology was studied by high-resolution scanning electron microscope (HR SEM) LEO Gemini 1550, equipped with INCA Energy/X-Max analyzer. Recycled powders were sampled after AM processing utilizing EBM process (Arcam A2 machine) and LS processing (EOS M290). Hastelloy X powder degradation was studied in case of LS process (EOS M290) and Alloy 718 powder was studied after EBM processing (Arcam A2X).

Results and discussion

Stainless steel powder

Stainless steel powder as 316L is still the main working horse in case of the laser sintering (LS) characterised by well-established process parameters and robust manufacturing window, supplied by all of the LS hardware manufacturing. This type of alloy has a very well established gas atomization technology for powder fabrication and hence 316L powder of very good quality, produced by variety of the gas atomisation techniques, can be acquired. Typical powder for AM, produced by VIGA, is characterised by very good purity from the surface composition point of view, see Fig.1. Powder surface is clean, there are no obvious particulate oxide phases present on the powder surface. Powder is covered by a by thin uniform iron oxide layer, ranging between 2 to 4 nm, depending on the powder manufacturing route. However, significant changes in the appearance of the powder surface are observed after EBM-processing, see Fig.2. Even though powder seems to be unaffected at low magnification, observation of the powder surface at higher magnification clearly shows appearance of the particulate features on the powder surface, sizing up to 200 nm, that are typically characterised by irregular shape. Enrichment in Cr, Mn and Si was also detected in the features based on the EDX analysis [9].

Detailed analysis of the powder surface chemistry by XPS analysis [9] indicate almost no change in the thickness of the iron oxide layer, covering powder surface – 2.9 nm in case of virgin powder and 2.6 nm in case of recycled powder. However, significant changes were observed in the relative fractions of cations for oxide phases on the powder surface, see Fig.3. In case of virgin powder, initial decrease in iron cation content with ion etch depth indicates removal of the iron oxide layer, while maintained level at greater etch depth is connected to the contribution from the un-etched regions on the powder surface. The increased levels of cation content of Mn and Cr until ~10 nm indicate presence of the fine particulates of similar size, also evident from high magnification SEM in Fig.1. In case of recycled powder, similar initial behaviour of the iron oxide content is evident, indicating similar thickness of the homogeneous iron oxide layer, covering most of the powder surface. However, for larger etch depths (>3 nm), situation is very different. Higher content in Cr-cation level is evident, indicating formation of the Cr-rich particulate oxides on the powder surface. The increase in relative Cr-cation content with etch depth, indicate that the thickness (and hence size) of the Cr-containing oxide products is greater than the final etch depth of 20 nm applied. This is in correlation with the SEM observations, see Fig.2, where particulate features sizing up to 200 nm are evident. The EDX analysis of these features confirms enrichment in Cr as well [9]. At the same time, decrease in Mn-cation content compared to that of virgin powder is observed. This is attributed to the Mn-sublimation during EBM processing as powder is kept at high temperature (around 800°C) in vacuum. The same counts for surface contamination of powder by Zn, present in the case of virgin powder but fully absent in case of EBM processed powder.

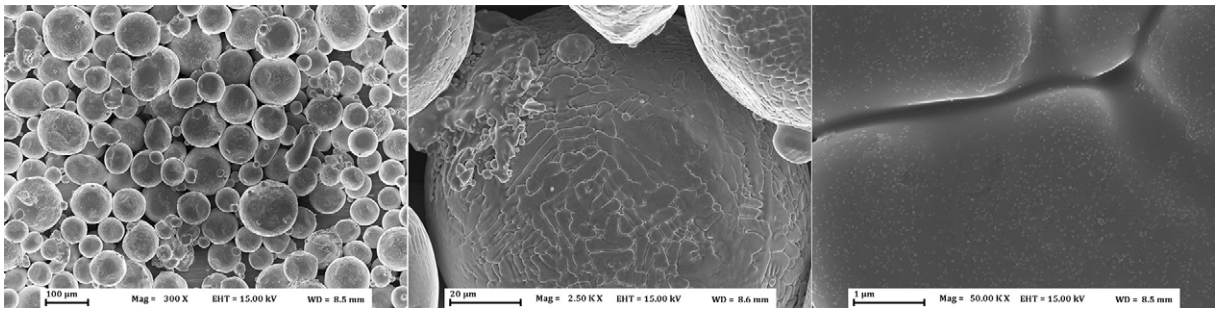

Fig. 1 - SEM micrographs of gas atomized stainless steel powder 316L (Fe-16Cr-10Ni-2Mo-2Mn-0.75Si), showing appearance the powder surface.

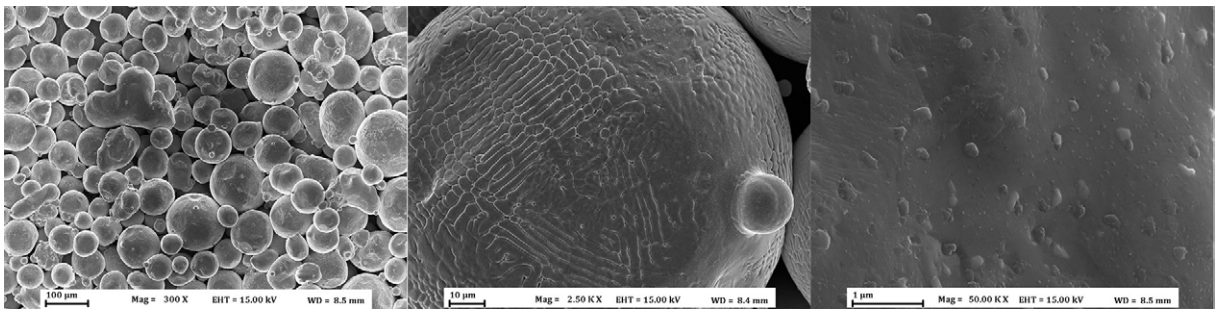

Fig. 2 - SEM micrographs of gas atomized stainless steel powder 316L after one EBM cycle (recycled powder), showing appearance of the particulate features on the powder surface.

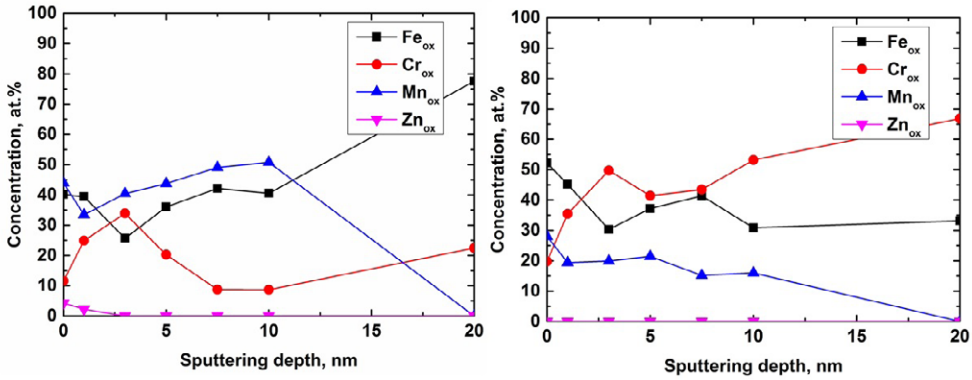

Fig. 3 - Relative cations concentration in oxide present on the surface of virgin powder vs. etch depth (left) and recycled powder vs. etch depth (right).

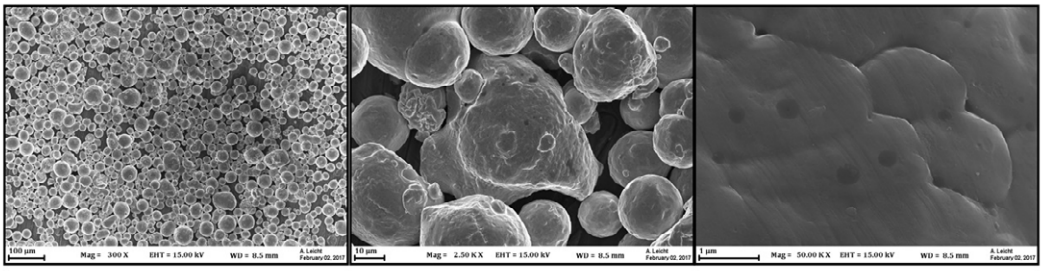

Fig. 4 - SEM micrographs of gas atomized stainless steel powder 316L after one LS cycle (recycled powder), showing appearance of the particulate features on the powder surface.

In case of laser sintering, see Fig.4, effect of the one cycle of processing by laser sintering on the powder surface chemistry is much less evident than in the case of EBM processing, see Fig.2. In general, powder surface seems to be un-affected and only in some places appearance of the spherical particulate sizing up to 200 nm can be observed. In this case, oxide particulates have a dark appearance and perfect spherical shape and are enriched in Mn and Si, based on EDX analysis.

Ni-base superalloy powder

Results for Hastelloy X powder, manufactured by vacuum induction gas atomisation (VIGA), are presented in Fig.5, indicating high surface purity of powder, characteristic for VIGA. From XPS, it is found that the powder surface is covered by a thin (around 1 nm) uniform nickel oxide/hydroxide layer with very rare presence of fine particulate features of thermodynamically stable Al-Cr-Ti-Si oxides [7]. However, the surface composition of the powder is significantly changed after laser sintering (LS) process. The SEM observation of the powder surface at high magnification clearly reveal extensive surface coverage by fine particulate features sizing around 20 nm, sporadically forming larger agglomerates on the powder surface, see Fig.6. The EDX analysis indicate that these features are rich in Cr and Al, see Fig.6. The XPS analysis, see Fig.7, confirms the strong presence of Cr and Al in oxidized form in the surface oxide products after LS-processing. Based on the presented results it can be concluded that powder surface after LS processing is enriched in thermodynamically stable oxides rich in Cr and Al. These oxide phases are very difficult to be removed during the rapid LS processing and hence can be detrimental for the mechanical performance of the final components.
However, sporadically much more oxidised metal particles can be found in the powder after LS-processing, see Fig. 8. Such metal particles were not observed in the virgin powder, their appearance already after processing in the laser sintering machine is at first strange. However, by sampling powder at the atmosphere outlet in the build chamber it was detected that almost all the powder there possess this type of oxidation, see Fig. 8. In case of fine particles (~20 μm) they are fully oxidised. In case of coarse powder particles with size about 50 μm they are oxidised from one side only. This is believed to be the powder from the interface between the volume of material scanned by laser beam and powder bed.

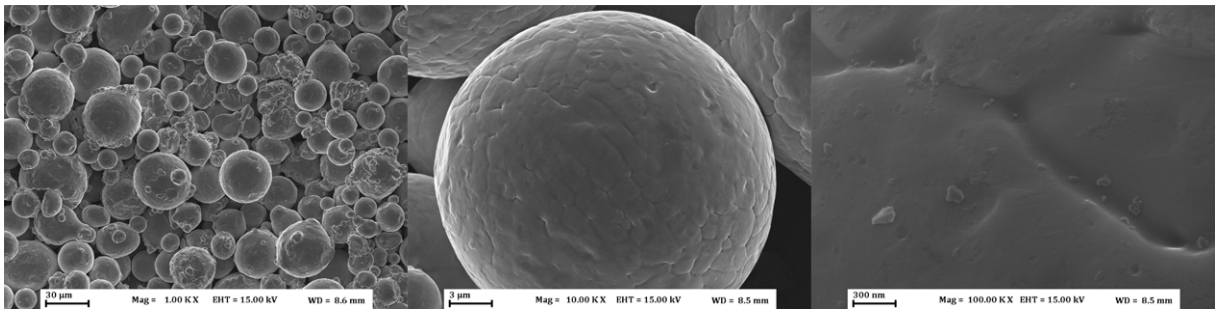

Fig. 5 - SEM micrographs of Hastelloy X powder, produced by VIGA in as-received state.

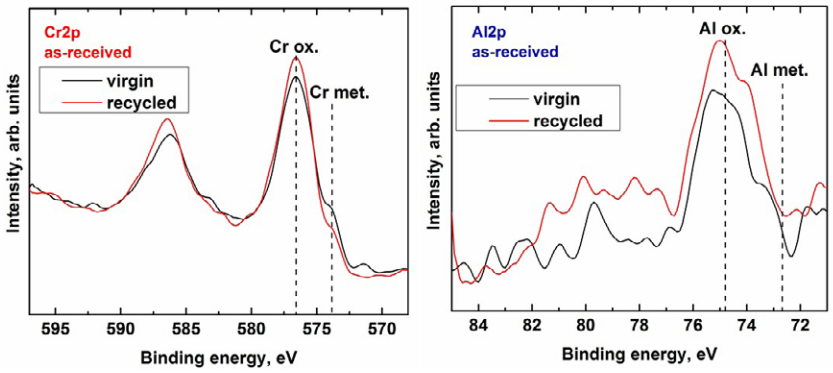

Fig. 6 - SEM+EDX analysis of the LS-recycled Hastelloy X powder.

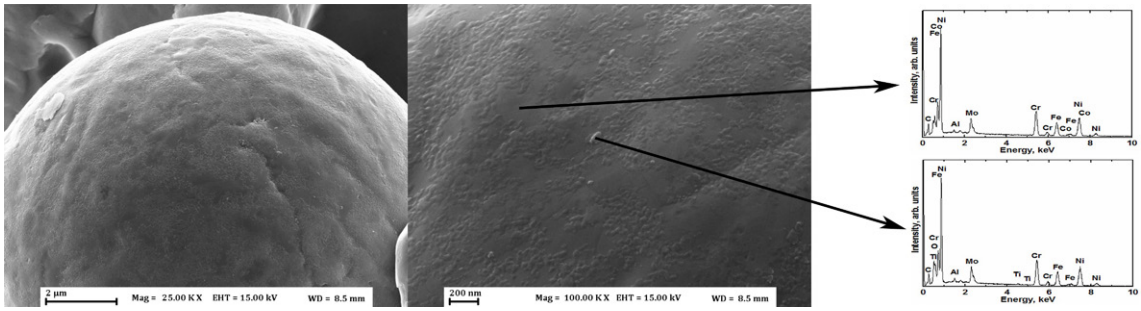

Fig. 7 - Detailed XPS spectra of Cr (left) and Al (right) on the surface of the Hastelloy X powder in virgin and recycled state, indicating larger oxide fraction in case of recycled powder.

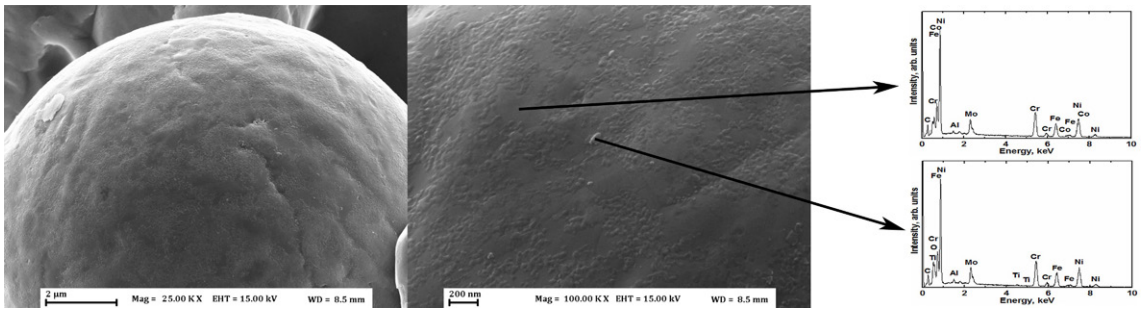

Fig. 8 - SEM+EDX analysis of the "burned" Hastelloy X powder, sampled after one LS-cycle close to the processing atmosphere outlet.

In case of electron beam melting it is typically expected that the issues with the powder recycling in connection to the powder oxidation are less critical as the powder bed is kept under high vacuum during the whole EBM process. However, observation of the powder surface in case of high-alloyed powder indicate presence of strong degradation of powder surface. Typically used in EBM process, like plasma atomised powder, is characterised by high purity, see Fig. 9, with visible dendritic structure and absence of pronounced formation of particulate oxide features on the powder surface. Analysis of the powder from the powder cake after EBM processing indicate though significant changes in the powder surface appearance as well as powder surface chemistry, see Fig. 10. Significant coverage of the powder surface by the fine particulate features is observed, increasing with the exposure time during the EBM processing. Even analysis of the powder from the powder hopper, not exposed to EBM process, but only exposed in the powder hopper for number of cycles, indicate appearance of the similar powder surface oxidation but to lesser extent. The reason for such powder degradation during EBM process is believed to be connected to the long-term exposure of the powder – dozens and even hundreds of hours – to the high temperature (about 1000 °C) and apparently not good enough vacuum to avoid powder oxidation. This preliminary study clearly indicates importance of the detailed study of the powder degradation during EBM processing.

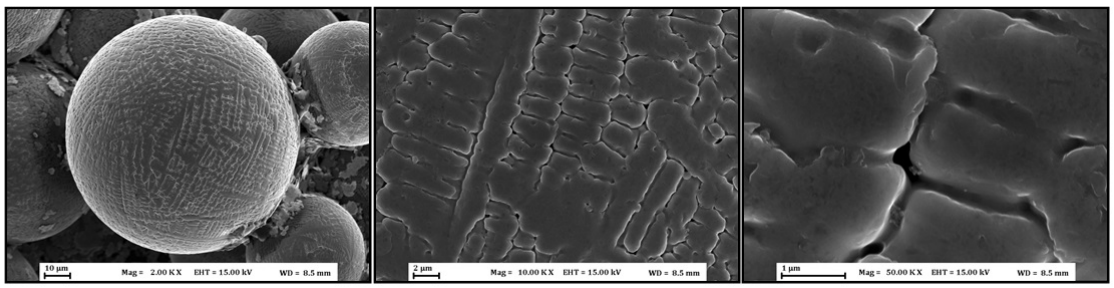

Fig. 9 - SEM micrographs of Alloy 718 powder, produced by plasma atomisation in as-received state.

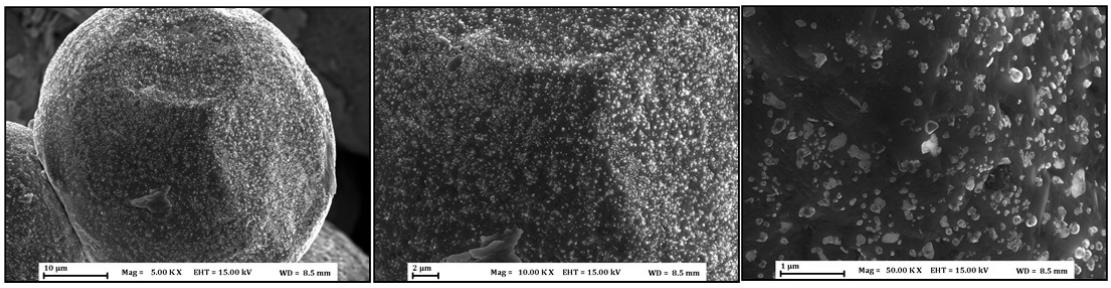

Fig. 10 - SEM micrographs of Alloy 718 powder after four cycles of EBM processing.

Conclusions

Combination of the advanced surface and microscopy techniques allows evaluation of the oxygen distribution in the powder as well as chemical composition of the specific oxide features, present on the powder surfaces. Powder for additive manufacturing is typically fabricated using advanced powder fabrication techniques as EIGA, VIGA or plasma atomisation and is characterised by spherical shape and high-purity. The powder is typically covered with homogeneous oxide layer formed by the main element (iron oxide in case of stainless or tool steels and nickel oxide/hydroxide in case of Ni-based superalloys). The thickness of the oxide layer is between 1 and 4 nm, depending on alloy composition, powder manufacturing method and powder handling. Rare presence of the particulate oxide features with size up to 20 nm, rich in oxygen-sensitive elements, can be observed.

Improper powder handling as well as processing by additive manufacturing techniques can lead to significant increase in surface coverage of the powder by thermodynamically stable oxides. Stainless steel powder shows rather minor changes in surface oxide state after laser sintering.

More significant coverage of the powder surface by the particulate oxide features is observed in case of 316L powder after EBM processing. Similar tendency is observed in case of Ni-based superalloys where rather extensive degradation of the powder surface was observed in case of EBM processing of Alloy 718 powder. In case of LS-processing, extensive degradation of some fraction of the powder was detected. Results indicate that combination of the advanced surface and microscopy analysis techniques the=e extent of the powder degradation during EBM and LS processing to be clearly determined and hence establish the limits of the powder recyclability.

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